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## (54) ACTIVE ENERGY BEAM-CURABLE COMPOSITION FOR PAPER COATING

(57)Abstract:

PURPOSE: To provide an active energy-curable type of resin composition for paper coating. which mainly comprises a specific oxetane ring-containing compound, thus shows a rapid curing rate and gives a coated layer having gloss, high adhesion, scuff resistance and flexibility.

CONSTITUTION: A compound having 1-4 oxetane rings in an amount of 100 pts.wt. is mixed with an optically cationic polymerization initiator such as a diaryl iodonium salt to prepare this composition for paper coating which is cured with active energy rays such as from a mercury lamp. This composition may be combined additionally with an alicyclic epoxy compound, a vinyl ether such as hydroxyethyl vinyl ether, a compound bearing (meth)acryloyl groups such as a (meth)acrylate ester of phenol, nonylphenol or ethyl hexanol and a photoradical polymerization initiator such as a benzoyl alkyl ether.

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#### DETAILED DESCRIPTION

[Detailed Description of the Invention] [0001]

[Industrial Application] This invention relates to the activity energy-line hardening setup-of-tooling product for paper covering which consists of a compound which has an oxetane ring, and the object for prizes is carried out in the field which manufactures and uses paper. In addition, in this specification, an acryloyl radical or a methacryloyl radical is expressed as an acryloyl (meta) radical.

[0002]

[Description of the Prior Art] While protecting its itself or printing side etc. on paper and raising blocking resistance, abrasion resistance, and abrasion-proof nature on it, coating processing may be performed to the front face in order to acquire gloss. Conventionally, approaches, such as the so-called vinyl length, a press coat, and a print lamination, were carried out to such processing. However, since these processing processes are accompanied by complicatedness, in recent years, the approach of using the activity energy-line hardening setup-of-tooling product which can stiffen a constituent for a short time is used. However, although unsaturated polyester, epoxy acrylate, or urethane acrylate hardened according to an activity energy-line initiation radical polymerization was used, generally, at the time of hardening, these had the large effect of the polymerization inhibition by oxygen for the application of several micrometer order and thin paper covering, and film thickness suited the inclination of activity energy-line hardening setup-of-tooling products [ most ] for the conventional paper covering which spoils the hardenability of a constituent, the abrasion-proof nature of the paint film obtained, etc. for it. [0003] As activity energy-line hardening techniques other than an activity energy-line initiation radical polymerization, the activity energy-line initiation cationic polymerization technique is put in practical use. Since especially activity energy-line initiation cationic polymerization is not checked by oxygen, there is no limit that it must carry out under an inert atmosphere, and it has the advantage that a prompt and perfect polymerization can be performed in air. The activity energy-line initiation cationic polymerization technique was concentrated on the polymerization of two kinds of monomers called an epoxy resin and vinyl ether till today. Especially a photoresist epoxy resin is excellent in an adhesive property, and the paint film has thermal resistance and good chemical resistance. However, in the conventional photoresist epoxy resin, since it had the defect in which a photopolymerization rate is comparatively slow, it was not able to be used in the application asked for prompt photo-curing. Moreover, the photoresist epoxy resin had that flexibility was not enough, when it was used for the application of paper covering. On the other hand, it is volatile, or there are many strong things of an odor, the contraction at the time of hardening is accepted as compared with photoresist epoxy, and photoresist vinyl ether has many which have not enough adhesion. [0004]

[Problem(s) to be Solved by the Invention] this invention persons inquired wholeheartedly in order to find out the activity energy-line hardening setup-of-tooling product for paper covering which solves these problems and which it excels in hardenability, and the paint film has gloss, and is further excellent in adhesion, abrasion-proof nature, and flexibility.

### [0005]

[Means for Solving the Problem] this invention persons completed header this invention for the ability of the constituent which consists of cyclic ether which has specific structure by various examination to solve the above-mentioned technical problem as a constituent for activity energy-line hardening molds for paper covering. Namely, the activity energy-line hardening setup-of-tooling product for paper covering which consists of a compound with which the 1st invention of this invention has 1-4 oxetane rings, and an optical cationic initiator, The activity energy-line hardening setup-of-tooling product for paper covering of the 1st invention which contains further the compound with which the 2nd invention has an epoxy group, The activity energy-line hardening setup-of-tooling product for paper covering of the 1st invention which contains further the compound with which the 3rd invention has a vinyl ether radical, or the 2nd invention, The 4th invention is the activity energy-line hardening setup-of-tooling product for paper covering of the 1st invention which contains further the compound and the optical radical polymerization initiator which have an acryloyl (meta) radical, the 2nd invention, or the 3rd invention. Hereafter, this invention is explained to a detail.

[0006] O The compound which has the oxetane ring used by compound this invention which has 1-4 oxetane rings has 1-4 oxetane rings. When the compound which has five or more oxetane rings is used, flexibility is lost by the hardening film of a constituent and a cracking crack may be caused by bending. Various things can be used for it if the compound which has the oxetane ring used by this invention is a compound which has 1-4 oxetane rings. As a compound which has one oxetane ring, the compound shown by the following general formula (1) is mentioned.

[0008] It sets at a ceremony (1) and is R1. They are the alkyl group of 1-6 carbon numbers, such as a hydrogen atom, a methyl group, an ethyl group, a propyl group, or butyl, the fluoro alkyl group of 1-6 carbon numbers, an allyl group, an aryl group, a furil radical, or a thienyl group. R2 The alkyl group of 1-6 carbon numbers, such as a methyl group, an ethyl group, a propyl group, or butyl, 1-propenyl radical, 2-propenyl radical, a 2-methyl-1-propenyl radical, The alkenyl radical of 2-6 carbon numbers, such as a 2-methyl-2-propenyl radical, 1-butenyl group, 2-butenyl group, or 3-butenyl group, The radical which has rings, such as a phenyl group, benzyl, fluoro benzyl, a methoxybenzyl radical, or a phenoxy ethyl group, The alkyl carbonyl group of 2-6 carbon numbers, such as an ethyl carbonyl group, a propylcarbonyl radical, or a butyl carbonyl group, The alkoxy carbonyl group of 2-6 carbon numbers, such as an ethoxycarbonyl radical, a propoxy carbonyl group, or a butoxycarbonyl radical, Or it is N-alkyl carbamoyl group of 2-6 carbon numbers, such as an ethyl carbamoyl group, a propyl carbamoyl group, a propyl carbamoyl group, a propyl carbamoyl group, a butylcarbamoyl radical, or a pentyl carbamoyl group, etc.

[0009] Next, as a compound which has two oxetane rings, the compound shown by the following general formula (2) is listed.
[0010]

[Formula 2] 
$$R^1$$
  $O$   $R^3$   $O$   $R^1$  (2)

[0011] It sets at a ceremony (2) and is R1. It is the same radical as the thing in said general formula (1). R3 For example, they are the alkylene group containing lines, such as lines, such as ethylene, a propylene radical, or a butylene radical, or a branching-like alkylene group, a poly

(ethyleneoxy) group, or the Pori (propyleneoxy) radical, or a branching-like Pori (alkyleneoxy) radical, a pro PENIREN radical, a methyl pro PENIREN radical, or a butenylene radical, or a branching-like unsaturated hydrocarbon radical, a carbonyl group, and a carbonyl group, an alkylene group containing a carboxyl group, or an alkylene group containing a carbamoyl group. Moreover, R3 It is also the polyad chosen from the radical shown by the following type (3), (4), and (5).

[Formula 3] 
$$CH_2$$
 (3)

[0013] It sets at a ceremony (3) and is R4. The alkyl group of 1-4 carbon numbers, such as a hydrogen atom, a methyl group, an ethyl group, a propyl group, or butyl, They are halogen atoms, such as an alkoxy group of 1-4 carbon numbers, such as a methoxy group, an ethoxy radical, a propoxy group, or a butoxy radical, a chlorine atom, or a bromine atom, a nitro group, a cyano group, a sulfhydryl group, a low-grade alkyl carboxyl group, a carboxyl group, or a carbamoyl group.

[0014]

$$[Formula 4] - CH2 - CH2 - CH2 - (4)$$

[0015] a formula (4) -- setting -- R5 An oxygen atom, a sulfur atom, a methylene group, NH, SO and SO2, and C (CF3)2 Or C(CH3) 2 it is . [0016]

[0017] It sets at a ceremony (5) and is R6. They are the alkyl group of 1-4 carbon numbers, such as a methyl group, an ethyl group, a propyl group, or butyl, or an aryl group, n is the integer of 0-2000. R7 They are the alkyl group of 1-4 carbon numbers, such as a methyl group, an ethyl group, a propyl group, or butyl, or an aryl group. R7 It is also the radical chosen from the radical shown by the following formula (6).

[0018]  
[Formula 6]  

$$R^8$$
  $R^8$   
 $-O - (Si - O) - Si - R^8$   
 $R^8$   $R^8$  (6)

[0019] It sets at a ceremony (6) and is R8. They are the alkyl group of 1-4 carbon numbers, such as a methyl group, an ethyl group, a propyl group, and butyl, or an aryl group. m is the integer of 0-100. As an example of a compound of having two oxetane rings, the compound shown by the following formula (7) and (8) is mentioned.

[0020] [Formula 7]

[0021] It sets at a ceremony (2) and the compound shown by the formula (7) is R1. An ethyl group and R3 It is the compound which is a carboxyl group.

[0022]

[Formula 8]
$$\begin{array}{c|c}
CH_3 & CH_3 \\
 & | \\
Si - O \\
 & | \\
CH_3 & | \\
Si \\
 & | \\
CH_3
\end{array}$$
(8)

[0023] It sets to a general formula (2) and the compound shown by the formula (8) is R1. An ethyl group and R3 are R6 at a formula (5). And R7 They are a methyl group and the compound whose n is 1. [0024] In the compound which has two oxetane rings, there is a compound shown by the following general formula (9) as desirable examples other than the above-mentioned compound. It sets at a ceremony (9) and is R1. It is the same radical as the thing in said general formula (1). [0025]

[0026] As a compound which has 3-4 oxetane rings, the compound shown by the following general formula (10) is mentioned.

[0027]
[Formula 10]
$$\begin{bmatrix}
R^1 \\
O
\end{bmatrix}$$
(10)

[0028] It sets at a ceremony (10) and is R1. It is the same radical as the thing in said general formula (1). R9 For example, the following type (11) Branching-like polysiloxy radicals, such as a radical shown by a branching-like Pori (alkyleneoxy) radical or the following formulas (15), such as a branching-like alkylene group of the carbon numbers 1-12, such as a radical shown by - (13), and a radical shown by the following formula (14), etc. are mentioned. j is 3 or 4.

[Formula 11]
$$CH_2 R^{10}-C-CH_2 CH_2-$$
(11)

[0030] In [type (11), R10 is low-grade alkyl groups, such as a methyl group, an ethyl group, or a propyl group.]
[0031]
[Formula 12]

$$\begin{array}{c}
CH_2 - \\
- CH_2 - C - CH_2 - \\
\vdots \\
CH_2 - 
\end{array} (12)$$

[0032]

[Formula 13]  

$$- \text{CH}_2 - \text{CH}_2 - \text{CH} - \text{CH}_2 -$$

[0033]

[Formula 14]

$$CH_{2} - (OCH_{2}CH_{2})_{1}$$

$$-(-CH_{2}CH_{2}O)_{1} - CH_{2} - C - CH_{2}CH_{3}$$

$$CH_{2} - (OCH_{2}CH_{2})_{1}$$

$$CH_{2} - (OCH_{2}CH_{2})_{1}$$

$$(14)$$

[0034] In [type (14), 1 is the integer of 1-10.]

[Formula 15]

[0036] As an example of a compound of having 3-4 oxetane rings, the compound shown by the following formula (16) is mentioned.

[0037]

[Formula 16] 
$$\begin{array}{c} CH_3 \\ | \\ Si - O \\ | \\ CH_3 \end{array}$$
 (16)

[0038] Furthermore, as an example of the compound which has 1-4 oxetane rings except having described above, there is a compound shown by the following formula (17). [0039]

[0039]
[Formula 17]
$$R^{11} = O = \begin{bmatrix} R^8 \\ S_1 \\ S_1 \\ C_1 \end{bmatrix} = O = \begin{bmatrix} R^{11} \\ C_1 \\ C_2 \end{bmatrix}_3$$
[17)

[0040] It sets at a ceremony (17) and is R8. It is the same radical as the thing in a formula (6). R11 is the alkyl group or trialkylsilyl groups of carbon numbers 1-4, such as a methyl group, an ethyl group, a propyl group, or butyl, and r is 1-4.

[0041] There is a compound shown below as a desirable example of the oxetane compound used by this invention.

### [0042]

[Formula 18]

[0043]

[0044]

[Formula 20]

[0045]

[0046] Moreover, the compound which has 1-4 oxetane rings which have the with a molecular weight of about 1000 to 5000 amount of macromolecules besides these is also mentioned. The following compounds are mentioned as these examples. [0047]

[Formula 22]

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[0048] Here, p is 20-200.

[0049]

[Formula 23]

[0050] Here, q is 15-100.

[0052] Here, s is 20-200.

[0053] O Various things can be used as an optical cationic initiator used with the constituent of optical cationic initiator this invention. A diaryl iodonium salt and a triarylsulfonium salt are mentioned as a thing desirable as these initiators. A typical optical cationic initiator is shown below.

[0054]

[Formula 25]
$$R^{12} \longrightarrow I^{+} \longrightarrow$$

$$MX_{k+1}^{-}$$
(25)

[Formula 26]

## [0056]

[Formula 27]

$$\begin{bmatrix} & & & \\$$

# [0057]

[Formula 28]

$$\begin{bmatrix} R^{13} - \bigcirc \\ \end{bmatrix}_{2}^{MX_{k+1}^{-}} - S - \bigcirc \\ \end{bmatrix}_{2}^{MX_{k+1}^{-}} - R^{13} \end{bmatrix}_{2}$$

[0058] R12 is a hydrogen atom, the alkyl group of carbon numbers 1-18, or the alkoxy group of carbon numbers 1-18 among a formula, and R13 is a hydrogen atom, a hydroxyalkyl radical, and a hydroxy alkoxy group, and is a hydroxy radical preferably. M -- a metal -- desirable -- antimony -- it is -- X -- a halogen -- it is a fluorine preferably, and k is a metaled valence, for example, in the case of antimony, it is 5. As for an optical cationic initiator, it is desirable to contain at 0.1 - 20% of the weight of a rate to those total quantities, when making the compound which has the compound and/or vinyl ether radical which have an epoxy group further in this contain as opposed to the compound which has an oxetane ring, and it is 0.1 - 10 % of the weight more preferably. When not filling to 0.1% of the weight, hardenability becomes less enough, when exceeding another side and 20 % of the weight, light

(28)

transmission nature becomes poor, uniform hardening may not be able to be performed or the smooth nature on the front face of a paint film may be lost.

[0059] In addition, in each above-mentioned chemical formula showing the compound or the optical cationic initiator which has 1-4 oxetane rings, even if each radical expressed with the same notation which exists in 1 molecule is mutually the same, it may differ.

[0060] O Other components can be blended with the constituent of other compound this inventions if needed besides the above-mentioned indispensable component. The 2nd invention of this invention is an activity energy-line hardening setup-of-tooling product for paper covering containing the compound which has an epoxy group further in the constituent of the 1st invention. In this case, the cure rate of a constituent is further improvable by making an epoxy compound contain in a constituent. Various things can be used as a compound which has an epoxy group. For example, as an epoxy compound which has one epoxy group, there are phenyl glycidyl ether, butyl glycidyl ether, etc., and hexanediol diglycidyl ether, tetraethylene glycol diglycidyl ether, trimethylolpropane triglycidyl ether, bisphenol A diglycidyl ether, a novolak mold epoxy compound, etc. are mentioned as an epoxy compound which has two or more epoxy groups. It is desirable especially to use an alicyclic epoxy compound by this invention, for example, the compound shown below is mentioned.

[0062]

[0063]

[0064] In this case, as the blending ratio of coal of a compound which has an epoxy group, 5 - 95 weight section is desirable to the total quantity 100 weight section of the compound which has the 1-4 abovementioned oxetane rings, and the compound which has an epoxy group.

[0065] The 3rd invention of this invention is an activity energy-line hardening setup-of-tooling product for paper covering containing the compound which has a vinyl ether radical further in the constituent of the 1st invention. In this case, the cure rate of a constituent is further improvable by making the compound which has a vinyl ether radical contain in a constituent. Various things can be used as a compound which has a vinyl ether radical. For example, as a compound which has one vinyl ether radical, hydroxyethyl vinyl ether, hydroxy butyl vinyl ether, dodecyl vinyl ether, propenyl ether propylene carbonate, cyclohexyl vinyl ether, etc. are mentioned. As a compound which has two or more vinyl ether radicals, the cyclohexane dimethanol divinyl ether, triethylene glycol divinyl ether, the novolak mold divinyl ether, etc. are mentioned. In this case, as the blending ratio of coal of a compound which has a vinyl ether radical, 5 - 95 weight section is desirable to the total quantity 100 weight section of the compound which has the 1-4 above-mentioned oxetane rings, and the compound which has a vinyl ether radical.

[0066] The 4th invention of this invention is an activity energy-line hardening setup-of-tooling product for paper covering containing the compound and the optical radical polymerization initiator which have an acryloyl radical further (meta) in the constituent of the 1st invention. In this case, reforming of adjustment of constituent viscosity and the paint film degree of hardness of a constituent can be performed by making the compound which has an acryloyl (meta) radical contain in a constituent. (Meta) Various things can be used as a compound which has an acryloyl radical. For example, as a compound which has one acryloyl (meta) radical, the acrylate (meta) of the alkylene oxide addition product of these alcohol etc. is mentioned to the acrylate (meta) of a phenol, nonyl phenol, and 2ethylhexanol, and a list. (Meta) As a compound which has two acryloyl radicals, the di(meth)acrylate of the alkylene oxide addition product of these alcohol etc. is mentioned to the di(meth)acrylate of bisphenol A, isocyanuric acid, ethylene glycol, and propylene glycol, and a list. (Meta) As a compound which has three acryloyl radicals, the Tori (meta) acrylate of the alkylene oxide addition product of these alcohol etc. is in pentaerythritol, trimethylol propane and the Tori (meta) acrylate of isocyanuric acid, and a list, and the Pori (meta) acrylate of pentaerythritol and dipentaerythritol etc. is mentioned as a compound which has four or more acryloyl (meta) radicals. Moreover, acrylic monomer oligomer with conventionally well-known the urethane acrylate which uses a urethane bond as a principal chain, the polyester acrylate which uses an ester bond as a principal chain, the epoxy (meta) acrylate which added the acrylic acid to the epoxy compound etc. is mentioned. In this case, as the blending ratio of coal of a compound which has an acryloyl (meta) radical, 5 - 95 weight section is desirable to the total quantity 100 weight section of the compound which has the 1-4 above-mentioned oxetane rings, and the compound which has an acryloyl (meta) radical. An optical radical polymerization initiator is blended with a constituent in the 4th invention of this invention. Various things can be used as an optical radical polymerization initiator. As a desirable thing A benzophenone and its derivative, benzoin alkyl ether, 2methyl [4-(methylthio) phenyl]-2-morpholino-1-propanone, Benzyl dimethyl ketal, 1-hydroxy cyclohexyl phenyl ketone, 2-hydroxy - 2-methyl-1-phenyl propane-1-ON, alkyl phenylglyoxylate, a diethoxy acetophenone and 2-benzyl-2-dimethylamino-1-(4-morpholino phenyl)-1-butane -- non, acyl phosphine oxide etc. is mentioned to a list. As for the content of these optical radical polymerization initiators, it is desirable that it is 0.01 - 20 % of the weight to the compound which has an acryloyl (meta) radical.

[0067] Moreover, in this invention, one sort chosen from the compound which has the epoxy group described above to the constituent of the 1st invention, and the compound which has an acryloyl (meta) radical in the compound list which has a vinyl ether radical, or two sorts or more can also be blended. In this case, it is desirable to make into 5 - 95 weight section the compound which has 1-4 oxetane rings on the basis of the total quantity 100 weight section of a compound which has the compound which has the 1-4 above-mentioned oxetane rings which are hardenability components as these blending ratio of coal, the compound which has an epoxy group, the compound which has a vinyl ether radical, and (meta) an acryloyl radical.

[0068] Inerts like an inorganic bulking agent, a color, a pigment, a viscosity modifier, a processing agent, an organic solvent, and an ultraviolet-rays cutoff agent can be blended with the constituent of this invention in the amount to the hit 100 weight section of the hardenability component 100 weight section.

[0069] The photosensitizer other than an optical cationic initiator or/and an optical radical polymerization initiator can be added to the constituent of this invention, and the wavelength of UV field can also be adjusted to it. as the typical sensitizer which can be used in this invention -- Crivello -- what [J.V.Crivello, Adv.in Polymer Sci., 62, and 1 (1984)] are indicating is mentioned, and, specifically, there are a pyrene, perylene, an acridine orange, a thioxan ton, 2-chloro thioxan ton, a benzoflavin, etc. [0070] O the approach which especially the manufacture approach of the constituent of operation this invention is not limited, but is usually performed -- the indispensable component of this invention -- or it is obtained by accepting an indispensable component and the need, and stirring or mixing other components. The operation of the constituent of this invention should just follow the approach currently conventionally performed by covering of paper. for example, paper -- a base material -- carrying out --

the methods of application, such as a curtain flow coat, a roll coat, or a spray coat, -- or the approach of applying the constituent of this invention to paper, irradiating an activity energy line by the printing approaches, such as offset, gravure offset, or offset, and stiffening etc. is mentioned. The paper by which the front face other than the regular paper which can use the paper of the base material set as the object of this invention for various things, for example, uses a cellulose as a principal component was processed with polyethylene, a polyvinyl chloride, polypropylene, polyester, a polycarbonate, or polyimide is mentioned. Although what is necessary is just to also choose the thickness of the constituent of this invention suitably according to the application to be used, as desirable thickness, it is 1-20 micrometers, and is 1-5 micrometers more preferably. As an activity energy line, ultraviolet rays, an X-ray, an electron ray, etc. are mentioned. Various things can be used as the light source which can be used when making it harden by ultraviolet rays, for example, pressurization or a high-pressure mercury-vapor lamp, a metal halide lamp, a xenon lamp, an electrodeless discharge lamp, or a carbon arc lamp is mentioned. When making it harden with an electron ray, what various irradiation equipment can be used, for example, a cock loft WARUTOSHIN mold, a BANDE graph mold, or a resonance transformer mold is mentioned, and has 50-1000eV energy as an electron ray is desirable, and is 100-300eV more preferably. Since cheap equipment can be used in this invention, it is desirable to use ultraviolet rays for hardening of a constituent. [0071]

[Example] An example and the example of a comparison are given to below, and this invention is explained more concretely. In addition, the section in each following example is weight criteria. [0072] Stirring mixing of the following compound (33) (henceforth Component G) 4 section was carried out as the following compound (32) (henceforth Component A) 100 section which has the manufacture oxetane ring of an example 1- constituent and which has the two following oxetane rings as a compound, and an optical cationic initiator, and the activity energy-line hardening setup-of-tooling product for paper covering was manufactured. [0073]

[0075] - coating of the evaluation profit \*\*\*\* constituent was carried out by the thickness of 10 micrometers on art paper, this is repeated on condition that conveyor speed 10 m/min in under the high-pressure mercury lamp of 80 W/cm and a condensing mold to 10cm location, the bottom of a mercury lamp was passed, and it was made to harden The following evaluations were performed about the constituent and paint film which were obtained. The result is shown in the following table 2. [0076] O The count of pass (count of passage) until adhesiveness disappears from a front face on the hardenability above-mentioned hardening conditions estimated.

[0077] O an adhesion profit \*\*\*\* paint film -- JISK Adhesion was evaluated according to the X cut tape method of 5400.

In addition, O in Table 2, \*\*, and x show following semantics.

O: JISK The evaluation mark of 5400 are 10 or 8\*\*: JISK. The evaluation mark of 5400 are 6 or 4x: JISK. The evaluation mark of 5400 are 2 or 0 [0078]. O The paint film side was made into the table

for the paper covered with the constituent paint film of flexibility this invention, the bend test was performed using the mandril with a diameter of 10m, and viewing estimated the condition of the paint film of a flection. In addition, O in Table 2, \*\*, and x show following semantics.

O: -- \*\*: which does not almost have a crack -- [0079] as which a crack is regarded by whole x: a crack is looked at [ whole ] by the part O about the front face of a gloss profit \*\*\*\* paint film, the gloss in 60 include angles was measured with the glossmeter. In addition, O in Table 2, \*\*, and x show following semantics.

O: less than [\*\*:50-90%x:50%] [0080] exceeding 90% O -proof -- the abrasion of the paint film front face was carried out by abrasion nature steel wool #0000, it got damaged and the degree was observed by viewing.

In addition, O in Table 2, \*\*, and x show following semantics.

O: -- \*\*: to which a blemish sees and is hardly stopped -- x: to which a blemish sees and is stopped slightly -- many blemishes -- \*\*\*\* and \*\*\*\*\*\*\*\* [0081] The constituent was manufactured like the example 1 except having used the component of the presentation shown in two to example 7 table 1. The activity energy-line hardening setup-of-tooling product for paper covering was manufactured like the example 1 using the obtained constituent. About the obtained paint film, it evaluated like the example 1. Those results are shown in Table 2.

[0082] The constituent was manufactured like the example 1 except having used the component of the presentation shown in one to example of comparison 3 table 1. The activity energy-line hardening setup-of-tooling product for paper covering was manufactured like the example 1 using the obtained constituent. About the obtained paint film, it evaluated like the example 1. Those results are shown in Table 2.

[0083]

[Table 1]

	A	В	С	D	E	F	G	Н
実施例1	100						4	
実施例2	50	50					4	
実施例3			25		75		4	
実施例4	75					25	3	1
実施例 5	25			50		25	3	1
実施例6	50				25	25	3	1
実施例7	75			25			4	
比較例1					100		4	
比較例 2				75	25		4	
比較例3					75	25	3	1

[0084] In Table 1, several show the section each. Moreover, in Table 1, component B-H shows the following compounds.

[0085] - Component B [the bottom-type (34) compound which has three oxetane rings] [0086]

[Formula 34]

$$CH_3 CH_2 C + CH_2 - O$$

$$O$$

$$(34)$$

[0087] - Component C [the bottom-type (35) compound which has one oxetane ring] [0088]

[Formula 35]

$$(35)$$

[0089] - Component D [the bottom-type (36) compound which has two epoxy groups]

[Formula 36]

[0091] - Component E [the bottom-type (37) compound which has two vinyl ether radicals] [0092]

[Formula 37]

$$CH_2 = CH - O + CH_2CH_2O + CH_2CH_2$$
 (37)

[0093] - Component F [the bottom-type (38) compound which has two acryloyl radicals] [0094]

[Formula 38]

$$CH_2 = CHCO + CH_2 + OCCH = CH_2$$

$$O O$$

$$O$$
(38)

[0095] - Component H (bottom-type (39) compound [ which is an optical radical polymerization initiator ]])

[0096]

[0097]

[Table 2]

	硬化性 (パス)	密着性	柔軟性	光沢	耐擦傷性
実施例1	7	0	0	0	0
実施例2	6	0	0	0	0
実施例3	3	0	Δ	0	0
実施例4	6	0	0	0	0
実施例 5	2	0	0	0	0
実施例6	3	0	0	0	0
実施例7	2	0	0	0	0
比較例1	3	Δ	Δ	×	Δ
比較例 2	未硬化	_	_	_	_
比較例3	8	×	×	Δ	×

### [0098]

[Effect of the Invention] A cure rate is quick, the paint film has gloss, and is further excellent in adhesion, abrasion-proof nature, and flexibility, and the practicality of a paint film of the activity energy-line hardening setup-of-tooling product for paper covering of this invention is very high.

[Translation done.]